

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

D4

Philips J. Res. **49** (1995) 23-46

SURFACE PREPARATION AND PHENOMENOLOGICAL ASPECTS OF DIRECT BONDING

by JAN HAISMA, GIJSBERTUS A.C.M. SPIERINGS,
THEO M. MICHIENSEN and COR L. ADEMA

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

Various intrinsic and extrinsic parameters that play a role in the preparation of materials for direct bonding are discussed in this paper. The constitution of a material or a wafer can be described on the basis of its shape and its mechanical, chemical and physical surface finish. Subsurface damage is also of importance with respect to direct bonding applications. Different polishing strategies have been evaluated for polishing the surfaces of different materials to a finish suitable for direct bonding. Optical elements can be polished by means of mechanical polishing; refractory metals by means of dedicated mechanical polishing; III-V compounds by means of chemical polishing; semiconductors by means of tribochemical, i.e. chemo-mechanical polishing; hard materials by means of enhanced tribochemical polishing; noble metals by means of organo-liquid-supported tribochemical polishing; non-noble metals by means of oxidation-stimulated polishing. After such preparative treatments the material or wafer has to be cleaned, using a suitable method. Certain aspects of the bonding phenomenon itself will also be discussed in this paper.

Keywords: direct bonding, surface finish, polishing strategy, cleaning, bonding phenomena.

1. Introduction

From a phenomenological point of view, a spontaneous direct-bonding process can be described as follows:

- (1) the wafers to be bonded are positioned parallel, e.g. on top of one another, in a wafer-bonding apparatus as shown in ref. [1];
- (2) gravitational forces, or forces intentionally applied to some part of the surface, cause the wafers to approach one another to within such a short distance that 'long range' attractive forces start to draw the surfaces together;

- (3) at a critical distance of some tenths of a nanometre the surfaces snap together. In recent experiments in which needles were bonded to surfaces in atomic-force microscopes (AFM) [2] this process was referred to as 'adhesive avalanche'. It is characterized by a structural shape transition from a system possessing two surfaces to a state with no identifiable surfaces [3];
- (4) in this adhesive avalanche an initially small bonded area is formed in which the surfaces are in atomic contact. As larger parts of the surfaces are drawn together the size of the bonded area grows at a constant rate (the bond-front or contact-wave velocity) [4] and in the process air is expelled from the gap between the two substrates. Variations in the flatness of the surfaces lead to adaptations in the shape of the wafer.

From the phenomenological description of direct bonding given above it will be clear that the surface and subsurface states of the materials to be bonded are of prime importance. Various aspects of these states will be discussed in this paper.

2. Surface and subsurface states

Many aspects of surface states are of importance in direct bonding:

- geometrical shape;
- mechanical surface finish;
- chemical surface finish;
- physical surface finish; and
- subsurface damage.

All these aspects have been studied in detail for a few materials only, e.g. silicon and silica. The following discussion will be based on the results obtained for these materials.

2.1. Geometrical shape

For two substrates to bond over their entire surface areas, they must either be enantiomorphic (complementary in shape) on a nanometre level or one (or both) of the substrates must be sufficiently flexible to be able to adapt its shape to that of the other substrate.

Silicon wafers are relatively thin (~ 0.5 – 1 mm) in comparison with their diameters (100–200 mm). Because of the elasticity of silicon, it is virtually impossible to define the geometrical shape on the basis of the flatness of such wafers; that will depend entirely on how the wafer is attached to its

carrier. Therefore, parallelism, or rather the deviation from parallelism, is a good criterion for the definition of its geometrical shape. In an accompanying paper [1] we describe a dedicated technology for fabricating wafers with less than $0.01\text{ }\mu\text{m}$ deviation from parallelism, which is 1 part in 10^7 relative to the diameter of those wafers. Such superparallel surfaces are necessary in the case of thin SOI wafers that are to be prepared for direct bonding using only grinding and polishing techniques.

2.2. Mechanical surface finish

One of the most important criteria for direct bonding is the roughness or smoothness of the surface: the short-distance irregularities which are commonly expressed in a root-mean-square value (Talystep measurements)

$$R_{\text{ms}} = \sigma = \sqrt{\frac{1}{N} \sum_{i=0}^{N-1} Y_i^2} \quad (1)$$

where Y_i is the local (i) distance from the measured curve to the horizontal axis, positioned at the mean height value of the measured curve.

Abe *et al.* [5] investigated bondability as a function of the mechanical surface finish and indicated the strong dependence of the bond strength on the surface smoothness. For direct bonding R_{ms} has to be smaller than 2 nm, preferably around 0.5 nm, i.e. of the order of the diameter of an atom. The atomic-scale roughness is particularly important in the case of surfaces that are covered with OH groups which can form hydrogen bonds across the interface only at distances of the order of the diameter of an atom.

2.3. Chemical surface finish

The chemical surface state of silicon is an important subject in IC technology. It concerns the chemical constitution of the outer surface(s), including any (inorganic and/or organic) dopants and/or contaminants present on the surface. The types of contaminant present may be of importance with respect to fusing phenomena during annealing after direct bonding.

Silicon readily reacts with oxygen, which means that unless special precautions are taken silicon wafers will be covered with a (native) oxide layer with a thickness of a few nanometres.

Under ambient conditions, the surface of the wafers will be covered with adsorbed molecules and/or ions. If large quantities of OH groups are present, the surface will be hydrophilic. Hydrogen bonds may then be formed, which will play a specific role in the direct bonding process. The

surface can be rendered hydrophobic with the aid of special treatments, but those treatments have consequences for the bondability of the wafers [6].

Electrical effects or related effects are observed when silicon wafers are intentionally oxidized to create buried electrical surface states [7] in the order of 10^{11} states per cm^2 at the silicon/silica interface. These effects have an influence on the bond strength. Materials that are susceptible to corrosion by water, oxygen or CO_2 may need special treatment.

Many of the subjects touched upon above will be dealt with in greater detail later on.

2.4. Physical surface finish

Matters of importance with respect to the physical surface finish are surface defects, such as machining scar marks consisting of grooves, i.e. relatively long intrusions with depths of a few micrometres ($\sim 1-3 \mu\text{m}$), and faint scratches, which are often curved and have depths of only a few submicrometres ($\sim 0.1-0.5 \mu\text{m}$). Bulk defects may also be apparent at the surface: for example, monocrystalline materials may show growth striations, twinings and inclusions, while polycrystalline materials may show grain boundaries, pores, etc.

Epitaxial layers, especially relatively thick ones, may show spikes, local extensions of preferential growth, which are detrimental for direct bonding.

2.5. Subsurface damage

Surfaces that have been polished mechanically may show plastic deformations. Surfaces and subsurfaces are internally and/or crystallographically damaged during mechanical machining. The extent of surface and subsurface damage can be determined by means of wet-chemical etching. The roughening of the surface is a consequence of the greater chemical reactivity of the damaged crystalline structure.

3. Polishing

The polishing strategy to be used to polish a surface to the finish required for direct bonding ($R_{\text{ms}} \leq 2 \text{ nm}$) depends on the material; different materials require different strategies.

Important parameters in the polishing strategy are:

- the shape of the sample;
- the polishing machine used (for single- or double-sided polishing; the number of moving parts);

TABLE I
Polishing methods and their fields of application

Polishing method	Field of application
mechanical	optical elements
dedicated mechanical	refractory metals
chemical	III-V compounds
tribochemical	elemental semiconductors
dedicated tribochemical	superfinish polishing of elemental semiconductors
enhanced tribochemical	hard materials
organic-liquid-supported tribochemical	noble metals
oxidation-stimulated tribochemical	non-noble metals
polish-stop	for achieving a specific flatness
zero-removal-rate polishing	one-sided polishing in a two-sided process
recessed-area flat polishing	polycrystalline, difficult to control

- the movement of the sample over the polishing pad (adjustable);
- the polishing pad (various hardnesses) [8];
- the polishing slurry (ranging from purely mechanical to purely chemical);
- the polishing pressure (a variable parameter); and
- the polishing temperature, which is dependent on the duration of the polishing.

The main difference between polishing strategies used for general purposes and those used for surfaces to be polished to the superfinish necessary for direct bonding concerns the removal rate, which is very small ($< 1 \mu\text{m/h}$) to extremely small ($< 0.1 \mu\text{m/h}$). So, superfinishing is a final finishing step; the effects of any machining operations carried out before this final step must not interfere with the superfinishing process.

Most of the parameters mentioned above are interrelated to varying extents, but the parameter with the greatest impact is the type of polishing slurry used.

Table I lists the various polishing methods and their fields of application. The different methods will now be discussed in detail separately.

3.1. Mechanical polishing

Mechanical polishing is a very old polishing method that is still used today. Material is removed by a cutting action, which results in plastic deformations.

The polishing slurry used for this purpose consists of hard particles suspended in a chemically inert liquid.

This method is ideal for polishing (optical) elements with flat or spherical, i.e. point-symmetric, surfaces. The degree of smoothness that can be realized with this method (of an order of magnitude of 2 nm R_{ms}) is good in an optical respect, but in a physical respect it is extremely poor because of the plastic deformations that are formed in the polishing process.

Mechanical polishing is a very satisfactory method for optical applications for which (sub)surface damage has no adverse effects. It is still the most suitable method for polishing optical elements and mechanical parts.

3.2. *Dedicated mechanical polishing*

The particles used in mechanical polishing contact the surface to be polished at a high pressure and many scratches are formed in the process. The amount of scratching caused depends on the diameter and shape of the particles. The smaller the particles, the smaller the amount of scratching will be; particles of microcluster dimensions (smaller than 10 nm; clusters of about 1000 atoms or less) cause no scratches whatsoever. Nanoparticles, i.e. particles with diameters smaller than 100 nm, cause very little scratching because they are less hard. This suggests that the use of a combination of deionized water and nanoparticles and a purely mechanical polishing method can result in a surface finish which approaches that of a surface free of surface and subsurface damage. Experiments have shown that this is indeed possible. This specific type of mechanical polishing is called *dedicated mechanical polishing*.

In our search for a suitable polishing method for hard, tough materials such as refractory metals we performed several experiments with various chemomechanical and chemical polishing methods. All our efforts with these methods proved unsuccessful and we therefore decided to investigate mechanical polishing in some greater detail.

We will now briefly describe our experiments with tungsten and molybdenum surfaces.

In our first experiment, in which we polished polycrystalline bulk tungsten in several ways, we observed that the tungsten was anisotropically affected in mechanical/chemical polishing. We were unable to obtain a surface finish of the quality required for direct bonding. We then investigated the effects of purely mechanical polishing on a hard polishing pad and found that the required finish could be obtained by using polishing particles with smaller diameters. Satisfactory results were obtained with Al_2O_3 nanograins (mean diameter about 50 nm) suspended in deionized water (5 g/l) and a polishing

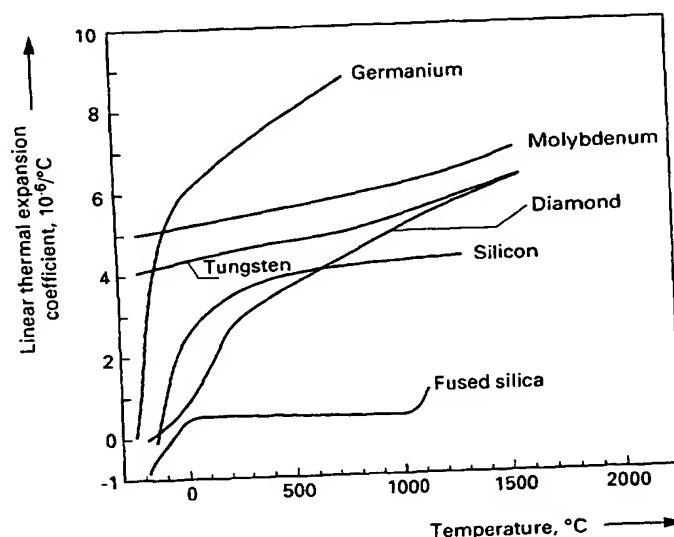


Fig. 1. Linear thermal expansion coefficients as a function of the temperature for Ge, Mo, W, diamond, Si and fused silica.

pad of (hard) pitch. We obtained a surface finish of a little below 2 nm R_{ms} . A sample of such a polycrystalline tungsten wafer proved to bond well to fused silica, that is, after a little pressure had been exerted.

Bulk polycrystalline molybdenum with properties resembling those of tungsten was also investigated. The results were more or less the same: the molybdenum bonded well to fused silica and silicon, but now the bond was formed spontaneously. The linear thermal expansion coefficients of W and Mo do not differ much from that of silicon, as can be seen in Fig. 1. This means that bonded wafer pairs can be subjected to various annealing treatments.

3.3. Chemical polishing

Polishing by means of purely chemical reactions can be applied to III-V compounds to a limited extent only. Chemical polishing has one important advantage: it causes no surface or subsurface damage. But it also has disadvantages. It is virtually impossible to obtain good geometrical results, and many of the chemicals used in chemical polishing, such as bromine and methanol, are toxic. In our chemical polishing experiments we succeeded in polishing InP to a level at which it could be directly bonded to a garnet. But the bond formed between the InP and the garnet was not very tight; the

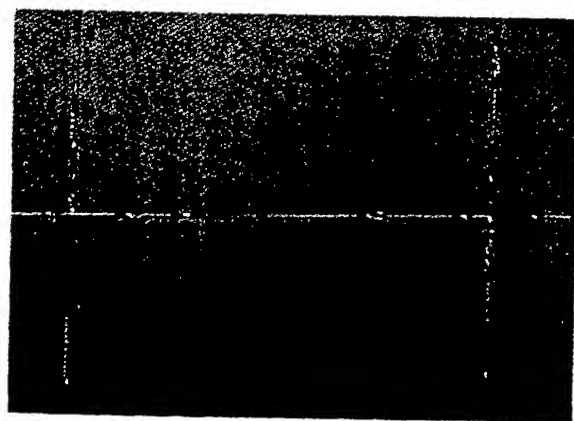


Fig. 2. Line-pattern laser-fused InP directly bonded to a garnet. Experimental conditions: Argon-ion laser radiation, $\lambda = 514$ nm; power 2–5 W; laser spot diameter in focus ~ 15 μm ; scanning speed 60 $\mu\text{m/s}$; trace distance 1000 μm .

directly bonded wafers had to be fixed to one another at points across their surface by means of laser fusion to prevent the risk of their becoming disconnected during further treatments. Figure 2 shows a planar view of such a bonded, laser-fused InP/garnet combination.

3.4. Tribochemical polishing

The development of polishing methods that do not involve the risk of damage to the polished surface is of great importance with respect to the manufacturing of semiconductors in particular. The surface properties of the electrically active materials to be used in integrated-circuit applications must remain intact over the entire wafer area. That is why much use is made of damage-free polishing methods in the silicon wafer industry. The standard polishing slurry consists of a colloidal suspension of nanoparticles of SiO_2 in an alkaline (NaOH , KOH) aqueous solution, commercially available under such tradenames as Syton (Monsanto) or Nalco (Rodel).

In the absence of additional mechanical forces these polishing media do not react with silicon and a passivating oxide layer is formed on the silicon [8]. The small particles, covered with reactive OH or O^- groups, are incorporated in the surface of the polishing pad. When this pad is then rubbed over the substrate surface, the mechanical forces at the nanoparticle interface increase the surface layer's reactivity towards water, which leads to the formation of temporary Si-O-Si bonds [9]. Soluble molecules containing silicon

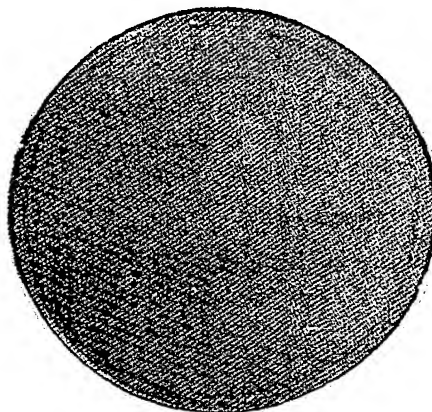


Fig. 3. ZnSe directly bonded to ZnSe after spontaneous bonding; diameter 20 mm.

atoms are formed, and in this process surface material is removed molecule by molecule.

Today, tribochemical polishing is widely used for polishing silicon and many other materials too, for example ZnSe. Figure 3 shows two directly bonded ZnSe wafers that had been tribochemically polished in a colloidal suspension of nanoparticles in an alkaline solution. The polished wafers bonded spontaneously after the first contact had been made.

3.5. Dedicated tribochemical polishing

When tribochemical polishing is used for elemental semiconductors, for example of Si or Ge, use is usually made of a colloidal SiO_2 suspension. Such suspensions ensure a high removal rate of at least $10 \mu\text{m/h}$, but the quality of the surface finish is not all that good (only about $2 \text{ nm } R_{\text{ms}}$).

A surface finish of a better quality can be obtained by using a polishing slurry with a different composition. An important chemical parameter of the slurry is the pH. Standard Syton slurries have a pH of 10, but for some surfaces a pH of about 7.5 is required. The pH can be lowered by adding an acid, e.g. HCl or H_3PO_4 . That results in an increase in the number of OH groups at the surface of the SiO_2 particles at the expense of O^- ions. The viscosity can also be altered; it can, for example, be increased by adding a substance such as glycerol.

We found a slurry containing 1000 ml Syton (Monsanto HT 50), 1000 ml

deionized water, 250 ml H_2O_2 (acting as an oxidizing agent) and about 175 ml glycerol, to which some HCl had been added to reduce the pH to 7.5, most suitable for obtaining a surface finish of the required high quality under our polishing conditions.

The method described above is called *dedicated tribochemical polishing*, i.e. dedicated to the realization of a surface finish of the high quality required. The removal rate of this method is rather low, however, i.e. $1\text{ }\mu\text{m/h}$ or less.

3.6. Enhanced tribochemical polishing

On several occasions we were asked about the possibility of realizing direct bonds between really hard materials such as diamond, more specifically the (100) crystallographic cut.

Diamond is the hardest material known today. The standard polishing method used for diamond is mechanical polishing using a slurry of diamond particles in water. This method indeed results in a mirror-like surface finish, but the surface and subsurface states are not of the quality required for direct bonding. We therefore decided to find out whether the finish required could be obtained using different polishing methods [10].

Our investigation showed that the surface finish in question can be obtained with the aid of a polishing method involving the use of:

- a polishing slurry of colloiddally suspended SiO_2 particles ($\sim 40\text{ nm}$) in an alkaline solution to which relatively few (about 1 g/l) diamond particles of small mean diameter ($0\text{--}1\text{ }\mu\text{m}$) are added;
- a polishing pad of pearlitic iron (with an open structure to enable a few of the diamond particles to be incorporated); and
- a polishing pressure of about 100 kPa (1 kgf/cm^2).

This method we have called *enhanced tribochemical polishing*.

Under the above polishing conditions the removal rate is extremely low, i.e. about one atomic layer per minute, but the surface finish ultimately obtained is about $0.5\text{ nm } R_{\text{ms}}$. Moreover, Rutherford backscattering spectroscopy revealed an almost complete absence of subsurface damage.

We assume that the following occurs during this polishing:

1. some of the small diamond particles are incorporated in the pearlitic pad;
2. both the embedded and the suspended diamond particles are encapsulated by SiO_2 nanoparticles due to Van der Waals forces; the particles retain their hardness, but no longer cause scratches;
3. the SiO_2 nanoparticles are largely covered with OH groups;
4. the OH groups are chemically very active;
5. the pressure at the contact points is very high;

Surface preparation and phenomena of direct bonding

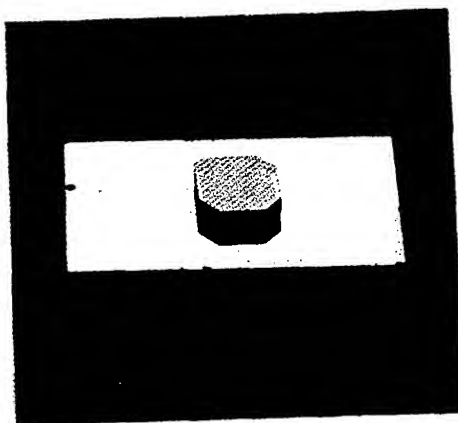


Fig. 4. Synthetic diamond ($4 \times 4 \times 2 \text{ mm}^3$), polished by an enhanced tribochemical method, bonded to silicon and annealed at 900°C in an atmosphere free of oxygen.

6. this combination of mechanochemical conditions causes carbon-carbon bonds to be broken;
7. the released carbon ions readily dissolve chemically in the alkaline medium, which leads to the result aimed at.

It should again be emphasized that this is a finishing method; it is not aimed at realizing a high removal rate.

Diamonds that had been polished with the aid of the above method proved to bond well to silicon (covered with a layer of native oxide) and the resulting bond could be annealed in an atmosphere free of oxygen at temperatures of up to 900°C . Figure 4 shows a synthetic diamond sample ($4 \text{ mm} \times 4 \text{ mm} \times 2 \text{ mm}$) polished, bonded and annealed as described above.

Other hard materials have been successfully polished in the same way, for example B_4C (polycrystalline), Al_2O_3 (monocrystalline) and AlN (polycrystalline); in each case the result was a surface suitable for direct bonding.

3.7. Organo-liquid-supported tribochemical polishing

The noble metals Pt, Au and Ag do not oxidize readily at room temperature and they are relatively soft. These two properties make it difficult to polish them to a superfinish.

Standard tribochemical polishing cannot be applied because of the noble materials' inherent resistance to oxidation, and mechanical polishing methods cannot be used because of the softness of the metals. That meant

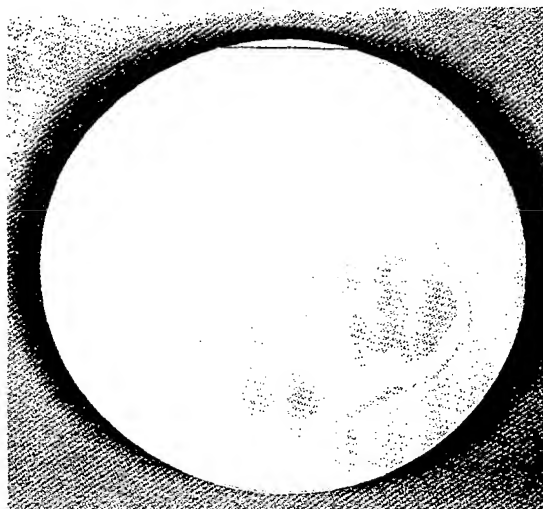


Fig. 5. Fused silica directly bonded to a platinum (rolled) wafer. The two surfaces bonded only after the application of some pressure.

that we had to develop a novel polishing method for the noble metals. The solution to the problem proved to involve the addition of organic molecules to the polishing slurry. Organic molecules chemically encapsulate the nanoparticles; the resulting slurry can be described as:

- a suspension of monocrystalline nanoparticles of between 0.1 and 1 wt% (e.g. Al_2O_3),
- having a Knoop hardness of between 5 and 50 GPa,
- in a mixture of deionized water and an organic liquid such as glycerol or some other polyalcohol, and
- having such a composition that complete encapsulation of the nanoparticles takes place.

The maximum polishing pressure to be used is 15 kPa (150 gf/cm²); the polishing pad is a tissue with a Shore A hardness [11] of between 10 and 80.

Figure 5 shows a fused-silica wafer directly bonded to a platinum disk. The bond could be realized under pressure only. Only the central part of the wafer is bonded to the disk. The platinum wafer was mechanically shaped by rolling; this is observable in the bonded pattern.

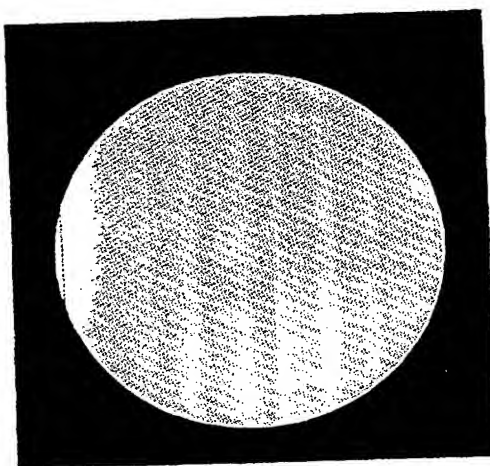


Fig. 6. Fused-silica wafer directly bonded to a copper plate; the bond was achieved under pressure; diameter 100 mm.

3.8. Oxidation-stimulated tribochemical polishing

Non-noble (base) metals oxidize in ambient atmosphere; like silicon, they have to be polished to a high-quality surface finish with the aid of tribochemical polishing methods. We extensively investigated one example, i.e. copper.

Copper cannot be polished to a bondable surface finish by means of straightforward tribochemical polishing using a suspension of nanoparticles of SiO_2 in an alkaline solution (Syton). We had to optimize the polishing method by adding H_2O_2 to the solution and then diluting it about 50% with water. The H_2O_2 enhances the oxidation of copper in the polishing medium. The oxide formed is immediately removed by the action of the polishing pad, which results in a smooth copper surface. This process closely resembles that which takes place during the superpolishing of silicon.

The polishing pressure was about 50 kPa (500 gf/cm²) and the polishing pad was a type of tissue. The copper thus polished could be bonded to fused silica and silicon. However, the bond had to be made under pressure (~ 5 GPa = 50 kgf/cm²) and the bonded area could be enlarged only by applying pressure to the entire wafer surface. In other words, it is possible, but very difficult, to bond copper directly to another material. Figure 6 shows a fused-silica wafer directly bonded to a copper plate (type of copper used: US ASTM: B152-84).

3.9. Polish-stop

For some technical applications an etch-stop or a polish-stop may be

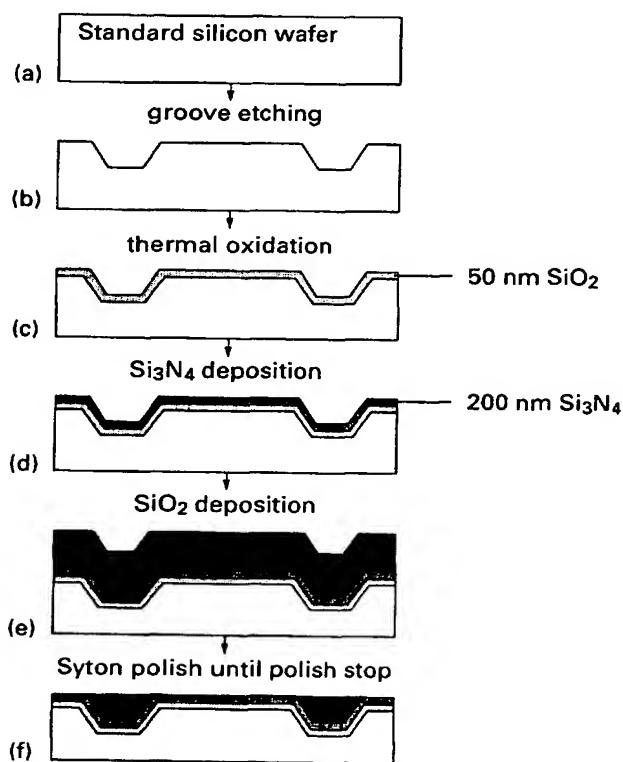


Fig. 7. Schematic representation of the various stages in the preparation of the active wafer for a polish-stop set-up before bonding for SOI applications.

required [12, 13]. In the case of a polish-stop a removal rate of almost zero is required for one of the surfaces to be polished, whereas a normal removal rate is required for the other surface.

We have performed experiments for silicon-on-insulator (SOI) applications; they are described in detail elsewhere [14]. The stopping medium used in our experiments was Si_3N_4 ; the material that was to be removed by means of tribo-chemical polishing was polycrystalline silicon (see Fig. 7).

3.10. Zero-removal-rate polishing

Some applications require wafers of which one side has been polished and the other has not. For example, for some SOI applications an oxidized silicon wafer (the handling wafer) is to be bonded to a second, almost

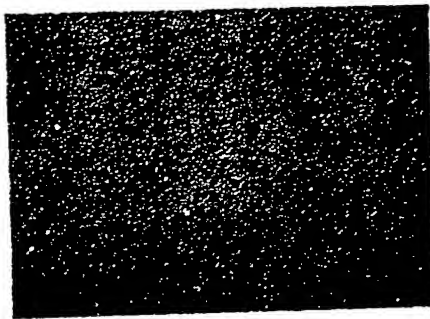


Fig. 8. Polycrystalline aluminium surface; finely ground.

parallel, oxidized silicon wafer, which is to be thinned (the device wafer). It has proved possible to obtain a homogeneously thin SOI layer by using a two-sided polishing machine, in which a zero removal rate is achieved for the handling wafer and a standard removal rate for the SOI device wafer [15].

Thermal oxide was used as the substance for which a zero removal rate was required and silicon as the substance to be polished. Different polishing pads were used for the different surfaces.

3.11. Recessed-surface polishing

The surfaces of tribochemically polished polycrystalline materials often include recessed areas. This is due to the fact that hardness and chemical reactivity are sometimes strongly dependent on the crystal orientation. If the surfaces have been well polished, however, the non-recessed areas will bond directly to, for example, fused silica; this phenomenon we have called *distributedly bondable*.

In a series of experiments we investigated the possibility of avoiding anisotropy in the polishing rate and obtaining a completely bondable surface.

The most striking results of these efforts are presented in figs. 8–10. Figure 8 shows a finely ground polycrystalline Al_2O_3 surface. It has no recessed areas, but is relatively rough and absolutely unsuceptible to direct bonding. Figure 9 shows the same surface after tribochemical, anisotropic polishing; the surface includes non-recessed and recessed areas. As already indicated above, the non-recessed areas are directly bondable.

It proved possible to modify the polishing process so as to give the surface with the recessed and non-recessed areas the appearance of a mechanically polished surface, i.e. a slightly scratched surface. The surface shown in Fig. 10 is clearly different from the surfaces shown in Figs. 8 and 9, but it is bondable.

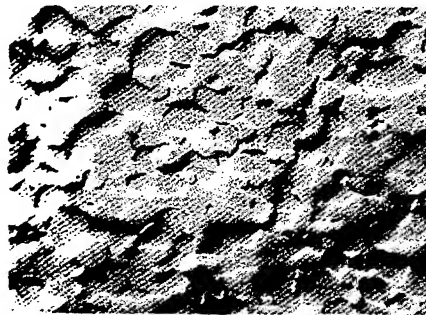


Fig. 9. Polycrystalline aluminium surface; same sample as in Fig. 8; tribochemically polished.

To conclude, the above results show that different polishing methods can be modified to render them suitable for polishing the surfaces of all kinds of materials to a finish suitable for direct bonding. However, developing a novel polishing method for a particular material is always a difficult and time-consuming exercise.

4. Surface preparation and cleaning

The surface conditions of materials that are to be directly bonded must be accurately controlled. These conditions comprise:

- the mechanical surface finish (roughness, smoothness),
- the chemical surface finish (e.g. hydrophobic, hydrophilic), and
- the cleanliness.

It proves to be quite difficult to control the above conditions in the case of some materials. We will restrict ourselves to some general comments below.

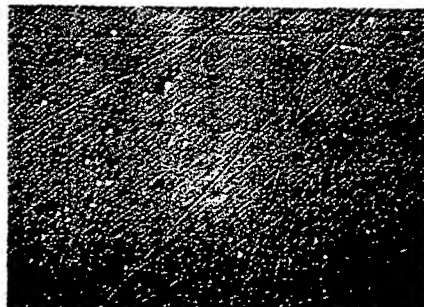


Fig. 10. Polycrystalline aluminium surface; same sample as in Fig. 8; mechanically polished.

Surface preparation and phenomena of direct bonding

Careful dedicated surface preparation by means of polishing is a prerequisite for obtaining a smooth surface with a low R_{ms} suitable for bonding. Direct bonds are formed only between surfaces that are free of impurities such as organic or inorganic particles and film-like adsorbents. Any contaminants present must therefore be removed. The cleaning method to be used for this purpose will, of course, depend strongly on the type of material to be cleaned. Strongly oxidizing liquids, such as aqueous solutions of $H_2SO_4-H_2O_2$ or $NH_4OH-H_2O_2$, are used to remove organic particles from inert materials, and a medium such as diluted HNO_3 can be used for removing inorganic particles. Scrubbing is often used as a final cleaning step. Scrubbing is the only possible method for removing adhering particles from reactive materials. The cleaned polished surfaces are dried by removing the adhering water with a pressurized air flow or by using the Marangoni drying method.

Surfaces intended for applications in which the bonded interface has to have specific, often electrical properties have to be free from adsorbed metal ions. This can sometimes be achieved with the aid of specific acids, such as diluted or fuming HNO_3 , but such media can be used only for cleaning sufficiently inert materials (such as silicon).

Cleaned, polished surfaces can optionally be treated to render the resulting hydrophilic surface hydrophobic. This can be achieved by dipping the surface into an HF solution or by means of high-temperature annealing [16]. A surface can also be chemically modified using organic silane compounds such as hexamethyldisilazane, if so desired.

5. Bonding phenomena

Direct bonding occurs under various external conditions related to the mechanical and chemical conditions of the surfaces. In investigating the tendencies of different materials to form direct bonds, we first tried bonding the materials to two well-studied, well-bondable substances, i.e. fused silica and silicon (natively oxidized). In a number of cases we then tried bonding the material to another surface of the same material.

Some materials were found to bond spontaneously, others bonded with difficulty. A material's tendency to form a direct bond is intrinsically related to the treatment to which it is subjected directly before bonding, i.e. polishing and/or cleaning, and to the geometry of its surface. As it is therefore dependent on many different factors it cannot be precisely specified. The gradual differences between various materials will be discussed first below, after which some general features will be outlined.

We classified the materials investigated on the basis of their tendency to

TABLE II
Materials that bond 'spontaneously' or 'perfectly'

First component of bonding experiment	Second component of bonding experiment		
	Silica	Silicon, natively oxidized	The same material
Mo (poly, bulk)	spontaneously	spontaneously	not investigated
Ta (poly, bulk)	perfectly	perfectly	perfectly
BaF ₂ (mono)	perfectly	well	well
SrTiO ₃ (mono)	spontaneously	spontaneously	well
ZrO ₂ :Y ₂ O ₃ (mono)	spontaneously	spontaneously	well
ZnSe (poly)	spontaneously	spontaneously	spontaneously
Polymethylmethacrylate (amorphous)	spontaneously	spontaneously	spontaneously

Bondability of chemical compounds:

- spontaneously: bond spontaneously on contact;
- perfectly: bond spontaneously after surfaces have been pressed into contact;
- well: bond well after the application of slight pressure.

form a direct bond. The classes of materials that were found to bond 'spontaneously', 'perfectly' or 'well' are shown in Table II. They were classified on the basis of the following observations.

Materials that bond 'spontaneously' are those that were found to form a direct bond immediately, without further intervention, when one wafer was placed on top of another. The bond-front velocity could be measured; in most cases it remained constant throughout the bonding process.

In the case of the materials that bonded 'perfectly' the first contact had to be brought about with the aid of some pressure, applied by hand, after which a bond was formed without further intervention. Typical bond-front velocities were a few cm/s.

In the case of the materials that bonded 'well' the first contact had to be brought about with the aid of some pressure, applied by hand, after which a bond was formed with the aid of some additional light pressure, applied by hand when necessary.

From Table III it is apparent that the majority of the materials investigated were found to bond well. Some polycrystalline materials proved to bond

Surface preparation and phenomena of direct bonding

distributedly; the only weak direct bond formed was that between two diamond surfaces. The latter bond was achieved under relatively high pressure.

Table IV shows that all the noble metals and copper bonded only with difficulty: a bond could be achieved only under a pressure of $\sim 5 \text{ GPa} = 50 \text{ kgf/cm}^2$ and the bonded area could be enlarged only by pressing the surfaces together. The bond-front velocity was found to be extremely low.

Two important aspects of direct bonding are:

- the first-contact phenomena, and
- the bond-front velocity.

The first-contact phenomena range from the spontaneous formation of a bond to the formation of a bond under substantial pressure. The differences shown by the different materials are probably related to the chemical properties of the surface layer. The bond that is formed between two surfaces that approach one another to within distances of a few nanometres is due to attractive forces such as Van der Waals forces. The relation between the attractive forces and the distance between the surfaces is quite complex; although it has been extensively studied and much insight has been obtained into the matter, it is still not completely understood.

A spontaneous bond is formed when the attractive forces increase smoothly, but substantially, as the surfaces approach one another. When the attractive forces show different behaviour, for instance if they transform into repulsive forces at a certain distance, the surfaces have to be pressed together to achieve a direct bond. The bond-front velocity, i.e. the rate at which the bonded area expands, depends on the chemical surface state and the type of material to be bonded.

The quality of the direct bond is determined by the bond energy and the associated bond strength.

We investigated the bond energy by inserting a wedge [17] between the bonded wafers and measuring the distance from the bond front to the wedge as a function of *the period for which the wafers had been bonded*. To this end we used a formula derived from the theory of crack propagation, which was developed by Gillis and Gilman [18] and applied to direct bonding by Maszara *et al.* [17]:

$$\tau = \frac{3Et^3y^2}{8L^4} \quad (2)$$

where τ is the bond energy, E is Young's modulus, t the thickness of the wafer, $2y$ the width of the crack (the thickness of the inserted wedge) and L the length of the crack (the distance between the bond front and the wedge). Figure 11

TABLE III
Materials that bond 'well'

First component of bonding experiment	Second component of bonding experiment		
	Silica	Silicon, natively oxidized	The same material
B (poly on SiO ₂)	well	well	well
Bi (poly, bulk)	well	well	not investigated
Ti (poly, bulk)	well	well	not investigated
W (poly, bulk)	well	well	not investigated
Ge (mono)	well	well	well
Si (mono)	well	well	well
B ₄ C (poly)	well	well	not investigated
C-C: = diamond (mono)	well	well	very weakly
Pyrolytic graphite	well	well	not investigated
CeF ₃ (on glass)	well	well	well
AlN (poly)	well (distributedly)	well (distributedly)	no bond formed
Si ₃ N ₄ (poly on Si)	well	well	no bond formed
YBa ₂ Cu ₃ O _{7-δ} (poly)	well	well	no
BaTiO ₃ (poly)	well	well	well
LiNbO ₃ (mono)	well	well	well

Surface preparation and phenomena of direct bonding

GaAs (mono)	well	well	well
InP (mono)	well	well	well
Polyarylate (sintered, bulk)	well	well	not investigated
Polycarbonate (bulk)	well	well	not investigated
Polyimide (bulk)	well	well	not investigated
Teflon (spin-coated on Si)	well	not investigated	not investigated

Bondability of organic materials:

- spontaneously: bond spontaneously on contact;
- well: bond well after the application of slight pressure.

TABLE IV
Materials that bond with difficulty only

First component of bonding experiment	Second component of bonding experiment		
	Silica	Silicon, natively oxidized	The same material
Ag (poly, bulk)	with difficulty	with difficulty	not investigated
Au (poly, bulk)	with difficulty	with difficulty	not investigated
Pt (poly, bulk)	with difficulty	with difficulty	not investigated
Cu (poly, bulk)	with difficulty	with difficulty	not investigated

shows the curve measured for a fused-silica wafer pair (diameter 10 cm, thickness $\approx 2 \times 525 \mu\text{m}$). It can be clearly seen that the bond energy increases in an exponential transient manner, reaching an asymptotic value for wafers that had been bonded for about 80 h. This is probably due to molecular or atomic rearrangements at the bonded interface, e.g. the formation of hydrogen bonds. The asymptotic bond strength measured for fused silica is 0.083 J/m^2 . A similar time-dependent bond strength behaviour was observed

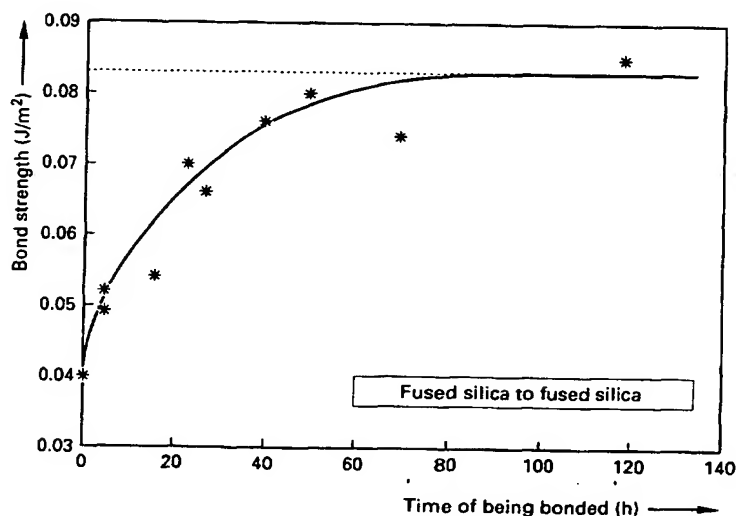


Fig. 11. Bond strength, measured by inserting a wedge between the bonded surfaces, as a function of the period for which the surfaces have been bonded. Example of a fused-silica wafer directly bonded to another fused-silica wafer.

Surface preparation and phenomena of direct bonding

for oxidized Si and silicon (in the case of silicon covered with native oxide bonded to silicon and in the case of a fused-silica wafer bonded to oxidized Si). The differences between the bond energies obtained for Si, SiO₂ and oxidized Si wafer pairs are presumably related to differences in elasticity. The bond energies obtained for hydrophilic Si and SiO₂ surfaces ranged from 0.05 to 0.20 J/m². We found similar bond energies for other materials with hydrophilic surfaces. Bond energies from 0.08 to 0.12 J/m² were measured within one hour after the formation of a direct bond between LiNbO₃ wafers and Si wafers, both with hydrophilic surfaces.

6. Conclusion

The most important step in the process of preparing materials for direct bonding is the polishing step, which determines the smoothness of the surface. After the surfaces have been polished, they have to be cleaned by a non-destructive method. It has been shown that existing polishing methods can be modified to render them suitable for polishing the surfaces of different materials to the finish required for direct bonding. Of great importance in the polishing process are the polishing slurry (i.e. its chemical composition and the type of particles suspended in it) and the polishing pad; different materials require different combinations of polishing slurry and polishing pad. In our experiments with different polishing methods we succeeded in achieving direct bonds between a wide range of different materials.

Acknowledgments

Mr Frank van der Kruis participated in the experiments. Our colleagues Rine Dona and Gerard Theunissen read the manuscript critically. Their contributions are gratefully acknowledged.

REFERENCES

- [1] J. Haisma, T.M. Michielsen and F.J.H.M. van der Kruis, Silicon wafer fabrication and (potential) applications of direct-bonded silicon, *Philips J. Res.*, **49**, 65–89 (1995).
- [2] J.S. Nelson, B.W. Dodson and P.A. Taylor, Adhesive avalanche in covalently bonded materials, *Phys. Rev. B*, **45**, 4439–4444 (1992).
- [3] K.-T. Wan, D.T. Smith and B.R. Lawn, Fracture and contact adhesion energies of mica–mica, silica–silica and mica–silica interfaces in dry and moist atmospheres, *J. Am. Ceram. Soc.*, **75**, 667–676 (1992).
- [4] G.A.C.M. Spierings and J. Haisma, Diversity and interfacial phenomena in direct bonding, *Proc. 1st Int. Symp. on Semiconductor Wafer Bonding, Science, Technology and Applications*, Phoenix, USA, 1992, Electrochemical Society, Pennington, USA, pp. 18–32.
- [5] T. Abe, M. Nakano and T. Itôh, in D.N. Schmidt (ed.), *Silicon-on-Insulator Technology and Devices*, Electrochemical Society, Pennington, USA, 1990, p. 61.

- [6] K. Ljungberg, A. Söderbärg and Y. Bäcklund, Spontaneous bonding of hydrophobic silicon surfaces, *Appl. Phys. Lett.*, **62**, 1362–1364 (1993).
- [7] D.R. Wolters and A.T.A. Zegers–van Duijnhoven, Thermal oxidation of silicon and residual fixed charge, *Microelectron. J.*, **24**, 333–346 (1993).
- [8] W.L.C.M. Heijboer, G.A.C.M. Spierings and J.E.A.M. van den Meerakker, Chemo-mechanical silicon polishing, *J. Electrochem. Soc.*, **138**, 774–777 (1991).
- [9] L.M. Cook, Chemical processes in glass polishing, *J. Non-Cryst. Solids*, **120**, 152–171 (1990).
- [10] J. Haisma, F.J.H.M. van der Kruis, G.A.C.M. Spierings, J.M. Oomen and A.M.J.G. Fey, Damage-free tribochemical polishing of diamond at room temperature: a finishing technology, *Prec. Eng.*, **14**, 20–27 (1992).
- [11] For a definition of Shore hardnesses, see DIN 53505.
- [12] K.D. Beyer, E. Mendel, W.A. Plishkin and J. Riseman, Glass planarization by stop-layer polishing, *IBM Tech. Disclosure Bull.*, **27**, 4700 (1985).
- [13] W.R. Morcom and Th.J. Sanders, US Patent 3 979 237, dated 7 Sept. 1976.
- [14] J. Haisma, G.A.C.M. Spierings, U.K.P. Biermann and J.A. Pals, Silicon-on-insulator wafer bonding–wafer thinning, technological evaluations, *Jpn. J. Appl. Phys.*, **28**, 1426–1443 (1989).
- [15] J. Haisma and F.J.H.M. van der Kruis, European Patent Application No. 0547 684; date of filing 10.12.92.
- [16] U. Gösele, T. Abe, J. Haisma and M.A. Schmidt (eds.), *Proc. 1st Int. Symp. on Semiconductor Wafer Bonding: Science, Technology and Applications*, Proc. Vol. 92–7, The Electrochemical Society, Pennington, USA, 1992.
- [17] W.P. Maszara, G. Goetz, A. Caviglia and J.B. McKitterick, Bonding of silicon wafers for silicon-on-insulator, *J. Appl. Phys.*, **64**, 4943–4950 (1988).
- [18] P.P. Gilles and J.J. Gilman, Double-cantilever cleavage mode of crack propagation, *J. Appl. Phys.*, **35**, 647–659 (1964).